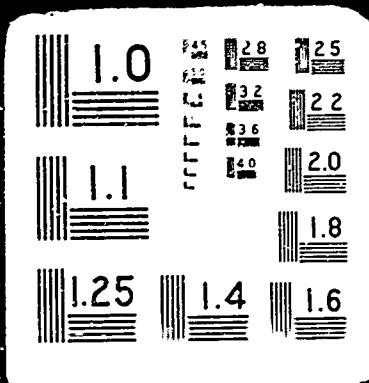


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**POTENTIOSTATIC CURRENT-POTENTIAL MEASUREMENTS
ON IRON AND PLATINUM ELECTRODES IN
HIGH-PURITY CLOSED ALKALINE SYSTEMS**

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ABSTRACT

Potentiostatic polarization curves were determined for Fe, Pt, and combinations of Fe and Pt electrodes in NaOH and LiOH solutions saturated with helium. With the high-purity, gastight system used, the level of reactable impurities was reduced to about 10^{-6} ppm. Under these conditions the primary reactions are, depending on potential, the oxidation or reduction of OH⁻ and water. Iron does not significantly corrode or show a decrease in reaction rate with an increase in potential (passivate). Iron acts like an inert noble metal similar to platinum.

Chloride ion causes extensive iron corrosion, completely changes the potentiostatic polarization behavior, and does cause typical passive behavior. Under high-purity conditions, iron is an excellent catalyst for the hydrogen oxidation reaction; the presence of chloride ion, however, almost completely destroys the catalytic properties of Fe for this reaction.

Unreactable and unremovable impurities such as carbonates, silicates, sulfates, apparently do not have major effects on the polarization behavior of Fe. The major anion, OH⁻, appears to dominate the inert anion effects.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem M04-08
ARPA Order 878

Manuscript submitted May 23, 1968.

POTENTIOSTATIC CURRENT-POTENTIAL MEASUREMENTS ON IRON AND PLATINUM ELECTRODES IN HIGH-PURITY CLOSED ALKALINE SYSTEMS

INTRODUCTION

Innumerable studies of the "passive" behavior of iron have been reported in the literature. Potentiostatic, steady-state investigations previously carried out on platinum electrodes, under conditions in which the rates of the electrode reactions were very slow, have shown that under such conditions reactable impurities can play a dominant role (1). It therefore seemed reasonable that, to carry out meaningful electrochemical studies of the behavior of an iron electrode under conditions in which the electrode processes occurred at very slow rates, impurities which can react or otherwise affect reaction rates in a primary way would have to be minimized.

To carry out such an investigation the high-purity, gastight electrochemical system developed at this Laboratory (2) was used. Measurements of reactable impurity levels in this system were shown to be equivalent to those found in a 10^{-12} -torr (1,2) vacuum system. To keep the iron electrode as inert as possible to corrosion, alkaline solutions were used.

A detailed explanation of the meaning of impurities should be made. By careful cleaning and aging of electrochemical cells and associated systems, the impurity level in solution can be kept low depending on the purity of the materials put into the cell. Further purification is possible by pre-electrolysis. Pre-electrolysis will remove species that deposit on an electrode, which can then be removed from the cell. In addition, certain species, in particular organic materials, can be removed by electrochemical oxidation or reduction. If the electrochemical system is a tightly closed one, then the level of impurities that can be removed by electrochemical means can be reached and maintained, limited by the rate of introduction of such impurities into the cell through leaks into the system or via materials (such as gases) introduced into the cell. Hence, the tighter the system, the more extensive the pre-electrolytic purification, and the better the purification of materials added during a run, then the lower will be the level of such impurities.

There always are, however, certain impurities which by our present technology are virtually impossible to remove below a certain level. For example, the electrode material itself always contains impurities. At the present time it is virtually impossible to reduce these to a level much below 1 ppm. Pre-electrolysis can largely remove reactable impurities at the surface. If the electrode is a solid at room temperature, the rate of diffusion of such impurities from the bulk of the electrode to the surface may be slow enough so that during a run their rate of arrival will be insignificant. Also, under the proper conditions, such impurities may react and be removed as the run is being made. Depending on the net rate of the particular reaction being studied, the effect of the impurity reaction may or may not be significant. In addition catalytic effects are possible.

Other possible sources of unremovable impurities in the electrolyte are the solvent, the chemicals which compose the solute, and the solution of species from the cell walls.

Note: This research was supported by the Advanced Research Projects Agency of the Department of Defense as part of ARPA Coupling Program on Stress-Corrosion Cracking (ARPA Order 878).

The amounts of such unremovable species may be maintained at a low level, but their complete removal is not, as yet, possible. The best one can hope for is that such impurities have secondary effects only on the electrode processes under investigation. In short, one can with present techniques reduce the level of reactable impurities to very low quantities (10^{-12} to 10^{-13} parts) and maintain these levels for long periods of time in a properly closed system (1,2). Unremovable impurities should be maintained at as low a level as possible by careful purification and selection of materials and by adsorption of impurities on large areas of inert materials. It should always be kept in mind, however, that any such adsorbents, no matter how inert they are, also do contribute impurities to the system. The really important consideration concerning unremovable impurities is how they affect the electrode process being studied. If the indications are that they do not significantly interfere, then they can be tolerated. For example, helium is an impurity often added to electrochemical cells so that an inert atmosphere is better maintained. Experience has shown that this impurity can be maintained at high levels without materially affecting electrode processes. Careful experimental design should always strive to keep the unremovable impurities to those species that do not have primary effects on the electrode process.

EXPERIMENTAL

The high-purity closed electrochemical system and the experimental conditions were essentially the same as those previously used (1,2). Before each run, the cell was cleaned with hot concentrated nitric acid and rinsed by continually distilling triply distilled water into it for at least 24 hours; finally, about 100 ml of water was distilled into the cell and cooled. The highest purity sodium hydroxide solutions (designated NaOH) were prepared by breaking in two a capsule of sodium metal, sealed under argon (99.95 percent with < 55 ppm heavy metals, with the major unremovable impurities being potassium, iron, calcium, silicon, magnesium, and carbon) and introducing the two halves into the cell in an atmosphere of purified helium. The two halves of the capsule were placed so the open ends were at the bottom of the cell. Thus as sodium metal dissolved, the hydrogen gas generated filled the capsule ends and regulated the introduction of water into the capsule. This allowed the sodium metal to react slowly.

Less pure sodium hydroxide solutions were prepared using a reagent-grade sodium hydroxide (97.4 percent pellets (designated NaOH pellets). The major unremovable impurities were Na_2CO_3 (0.64 percent), NaCl (0.003 percent) and silicate (0.01 percent). Lithium hydroxide solutions were prepared using lithium metal from two sources (99.99 percent and 99.92 percent). The unremovable impurities were primarily potassium, sodium, chloride, calcium, silicon, aluminum, and iron.

The working electrodes were Fe wires (fabricated from three-pass, electron beam zone refined iron with less than 4 ppm metallic impurities, 20-mil diameter, geometric area about 0.7 cm^2); a similar Fe wire with about 1 cm of 3-mil Pt wire spot welded to the Fe wire and wound around its tip (designated Fe >> Pt electrode); and a Pt wire (99.99 percent, 20-mil diameter, geometric area = 0.65 cm^2). Each was connected to Pt leads and sealed off in lead-free, soft glass tubes. The counterelectrode was a large Pt gauze electrode. The reference electrodes were in an arm off the main cell compartment and were a calibrated (vs Pt/H₂ in the same solution) miniature glass electrode and a Pd wire charged with hydrogen to a potential of about 50 mv more positive than a hydrogen electrode in the same solution. This Pd-H wire electrode was used as the potentiostatic reference.

Each solution was pre-electrolyzed for several days in a helium-saturated solution using a Pt pre-electrolytic cathode which was then removed from the cell. The purified helium flow was then replaced with a flow of hydrogen which was purified by passing through heated Pd-Ag tubes. The Pt wire, Pt gauze, and Pd wire potentials

were then determined against the glass electrode. After the Pt/H₂ electrodes reached their equilibrium values and the Pd-H wire was 50 mv positive to the Pt/H₂ potential an Fe wire (or Fe >> Pt), cleaned in 1-M H₂SO₄ and rinsed with triply distilled water, was introduced into the cell under an anodic-applied potential as the working electrode in the potentiostatic circuit. The glass reference electrode continuously monitored the potential on the Fe working electrode via a Keithley 610B electrometer. Current flow under potentiostatic conditions was determined with a Keithley 601 electrometer and recorded.

A point was determined on the potentiostatic polarization curve by holding the working electrode at a constant potential (calculated and recorded in reference to the normal hydrogen electrode (N.H.E.)) until a constant current was reached. The time required to reach a steady state varied from minutes to days depending on the potential and its sequence. The potential was then increased and the new steady-state current determined. This was continued until the potential was well into the oxygen generation region, after which the potential was made less noble in similar constant-current steps until the potential was well into the hydrogen generation region. Stepwise potential increases in the noble direction followed until a full potential cycle was achieved. The cycling continued until the current readings for consecutive cycles were consistent in value. These are the values given in the figures. It was found that several cycles, over a period of several weeks, were required before consistent polarization curves were attained. We believe that the inconsistencies in the initial cycles were due to traces of reactable impurities (primarily organic), which were slowly removed by oxidation. The temperature was 25 ± 2°C, and the flow rate of gas was normally 40 ml/min.

CHARACTERISTIC IMPURITY EFFECTS

During the pretreatment period, in which the potentiostatic current density vs potential varied considerably from cycle to cycle, certain characteristic behavior was observed which reflected decreases of reactable impurity levels in solution, from the electrode surfaces, and in the uppermost layers (derma) of the working electrode. In addition certain slow changes in the state of the working electrode surface and derma undoubtedly occurred. We are not, as yet, in a position to specify - or even to speculate on - the surface state of the iron electrode and the changes it undergoes as the potential is varied. However, under the high-purity conditions which were maintained after the pretreatment purification, the surface and derma states were consistently reproducible. The iron electrode itself underwent no visible change from the beginning to the end of a run (and some lasted for several months). The appearance of the iron did not indicate significant corrosion. Analysis of the solution at the end of a 3-month run gave about 0.1 μ g in the 50 ml of solution in the cell. Evidently the trace of iron that may come from the Fe electrode is so small that the anodic currents determined under potentiostatic conditions were primarily caused by OH⁻ and water oxidation rather than to Fe oxidation.

Figure 1 represents typical current density changes with time caused by a change in the working electrode potential. These show characteristic impurity behavior. Curve A, Fig. 1 typifies the smooth current-vs-time behavior found after the pretreatment cycle purification. Curve B is a synthesis which illustrates some of the abnormalities that may be caused by impurities found in a newly prepared electrolyte. Irregularities such as those shown at point 1 or false trends such as those found in the neighborhood of point 2 may occur.

Oscillations similar to those at point 3 may occur and tend to extend over the full length of the curve. Over fairly long intervals their frequency and amplitude are roughly constant. Oscillations may occur from one every few seconds to one every few minutes and may be so large that they obscure the base curve and make it difficult or impossible to determine the final reading for the constant current value. Oscillations of

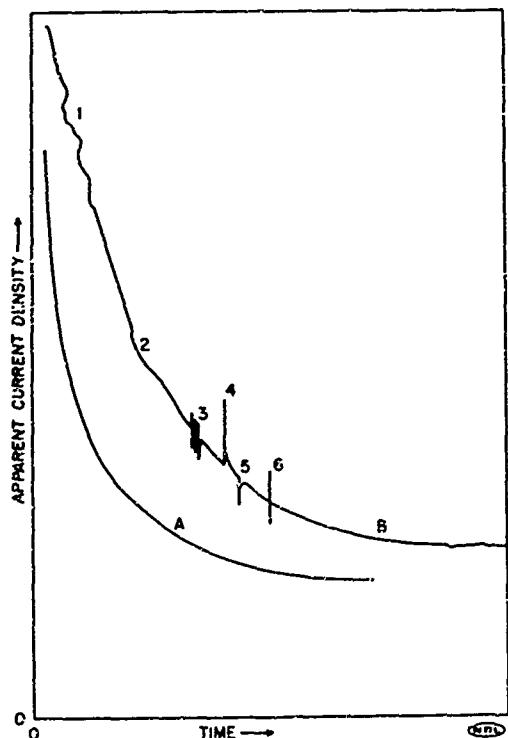


Fig. 1 - Typical current density changes with time following potential change; Curve A. Electrochemically purified system and Curve B. Types of abnormalities caused by impurities; "Numbers" 1-6 are explained in the text

this type have been induced in the pure Fe/NaOH system by the addition of small amounts of O_2 or Cl^- .

Impurities can cause sharp breaks in the current-vs-time curve such as those shown at points 4, 5, and 6 of Curve B, Fig. 1. Such changes in current generally occur quite rapidly and then return fairly slowly to the normal rate. Impurities that are reactable can contribute to the net current and can either sharply increase or decrease its value depending on whether they are oxidized or reduced.

For the purest Fe/NaOH system, at anodic currents, the number of coulombs passed from the start of the current-vs-time curve until the current becomes constant and is approximately equal to a fraction of a monolayer (two-electron reaction). This value is less for small potential steps and at potential settings that give relatively low current densities and is appreciably higher for large potential steps and at potentials which give high current densities. In comparing Curve B to Curve A in Fig. 1, it can be seen that the presence of reactable impurities increases the current at any given time and increases the time required for the current to become constant. Hence, when reactable impurities are present the total number of coulombs that flows can be much larger.

Another important characteristic of reactable impurities in solution is the stirring effect. The pure Fe/NaOH system under helium flow was essentially independent of the stirring rate (40 to 1000 ml He/min) except at the lowest current densities (10^{-9} amp/cm²). Reactable impurities gave substantial current differences at the highest stirring rate. The direction of such a current change depended on whether the current at slow He flow was anodic or cathodic and whether the impurity was being oxidized or reduced. Each of the effects shown in Fig. 1, Curve B has been induced by the addition of impurities such as Cl^- to a pure Fe/NaOH system.

Previous work (1) has shown that it is possible to estimate the amount of oxidizable or reducible impurities present in a purified system. This is done by introducing known trace amounts of hydrogen or oxygen to the helium flowing into the cell and observing the minimum amount required to change the steady-state current density at a sensitive (very low steady-state current density) set potential. Such measurements have been made for the systems investigated in this work, and it was shown that the conditions in which data were taken the minimum levels of oxygen or hydrogen to which the system was sensitive was approximately 10^{-6} ppm.

In addition to reactable impurities, which have been reduced to insignificant values in this work, the question of the effects of unremovable impurities must be considered. In the system used, one immediately becomes concerned with the presence of impurities that will dissolve from the Pyrex glass cell. These would primarily consist of silicate, borate, aluminate, sulfate, phosphate, and chloride. Our first reaction was to avoid alkali-to-glass contact in the cell by use of a Teflon coating or a noble metal cell. However, upon consideration of the total unremovable impurity problem it was soon realized that this would be an essentially useless complication. That is because similar amounts of the same impurities would remain in any cell. The level of such impurities is determined primarily by the unremovable impurities in the water, chemicals (Na, Li, NaOH) used to form the solution, the electrodes, and the impurities that come from the atmosphere (dust, etc.), which are virtually impossible to avoid in the assembly of any system. These impurities cannot at the present time be satisfactorily removed or even be reduced to levels significantly less than monolayer quantities.

In any case, the best we can do at present is to determine, as well as possible, whether such unremovable impurities do affect the electrode reactions of interest in a primary way. Using 99.95-percent sodium metal, 97.4-percent NaOH pellets, and 99.99 and 99.92-percent lithium metal in the preparation of solutions, we could compare data taken with each solution after the pretreatment purification procedures. The amounts of unremovable impurities varied considerably from solution to solution, but in all cases there undoubtedly were sufficient amounts of any of these impurities to form multiple monolayers if they deposited on the electrode surfaces. The actual data showed some significant differences, as will be discussed in this report, but the overall current density vs potential curve shapes and characteristics were fundamentally the same. It was felt that most of the unremovable impurities, such as silicates, borates, phosphates, and sulfates, would have little effect since adsorption of hydroxide would predominate in potential regions where the net charge on the electrode was positive. That is verified by the work of Pryor and Cohen (3) who showed that nonoxidizing anions had corrosion inhibiting effects very similar to those of the hydroxyl ion in the presence of air and that in the absence of air nonoxidizing anions do not inhibit iron corrosion. The most likely unremovable anion that may have important effects on electrode processes is chloride ion (and other halides), and most of the differences found for the varying purity of solutions used in this work can reasonably be laid primarily to the differences in chloride ion content. It was at the highest value for the sodium hydroxide pellets (0.003%), and this solution did give the widest variation in results from the purest solution studied. Work was done in which chloride additions (0.2 percent) did cause large differences in behavior and actual visual corrosion of the iron. This work will be reported below.

EXPERIMENTAL RESULTS

Figure 2 shows the potentiostatic polarization curves obtained under what is considered to be the purest conditions obtained. The electrolyte was prepared from 99.95-percent sodium metal and underwent extensive pre-electrolysis. In all the figures, the symbol Δ represents a steady-state current density made at a set potential that was higher than the potential of the previous reading (increasingly noble potential sequence). Conversely, the symbol \backslash indicates that the potential sequence was decreasingly noble.

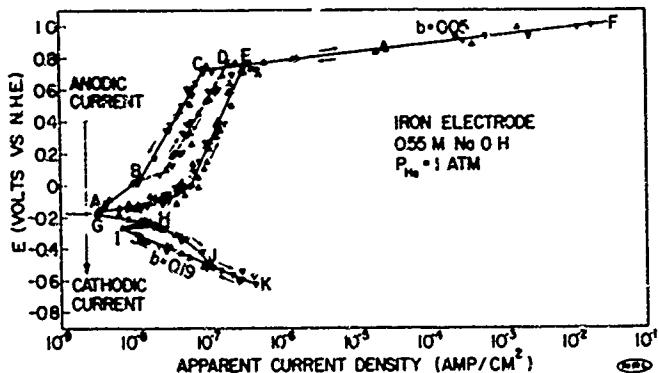


Fig. 2 - Fe potentiostatic polarization curves in 0.55-M NaOH; Δ increasing potential sequence, ∇ decreasing potential sequence, and letters A through K are explained in the text.

Curve AEF (Fig. 2) represents the increasing potential sequence data found when the initial potential was negative with respect to, or at, -0.17 v. The decreasing potential sequence starting at potentials positive with respect to 0.76 v (point E) gave data on curve FCA. If on the decreasing potential sequence FCA, the potential was taken to point B (0.04 v) and then a sequence of more noble potentials was applied, curve BDF was obtained. If on the increasing potential sequence, AEF, the most noble potential applied was 0.76 v (point E) and the potential was subsequently decreased, the data points fell on curve EDBA.

In any segment for which the arrow indicates the direction of change of the potential sequence, a reversal in potential gave a reading on that segment. This is indicated by Δ and ∇ data points for each curve segment in Fig. 2.

At point A and above the currents were anodic, while at point G and below they were cathodic. As the potential was made more cathodic below point G, the readings followed curve GHJK. Making the potential more noble in the region JK gave data points which followed curve KJHG.

The results shown in Fig. 2 were obtained for 0.55-M NaOH. Runs were made also at 0.30, 0.13, and 0.067-M concentrations. Such variations in concentration had little effect on the data shown, except for the segment CF. In this potential region, a decrease in alkali concentration resulted in a linear segment parallel to CF with the current densities being generally smaller as the solution was more dilute. Similar results were found with LiOH and other NaOH solutions.

The experiments depicted in Fig. 2 were repeated in a 0.2-M NaOH solution prepared from a different batch of high-purity sodium from the same supplier. The results are shown in Fig. 3, which includes data from Thomas and Nurse (4) taken in 0.1-M NaOH. Figure 4 shows the results obtained from a 0.58-M NaOH electrolyte prepared from reagent-grade NaOH (pellets).

An 0.85-M LiOH solution was prepared from high-purity metallic lithium (99.92 percent). The potentiostatic polarization curve is shown in Fig. 5. When this solution was diluted to 0.34-M LiOH, the change in this curve was negligible except in the linear $b = 0.04$ region, where the curve ran about 0.06 v higher. A 0.28-M LiOH solution was prepared from another pure lithium (99.99 percent) sample which contained about one fifth the amount of unreactable impurities as the lithium used in Fig. 5. The results

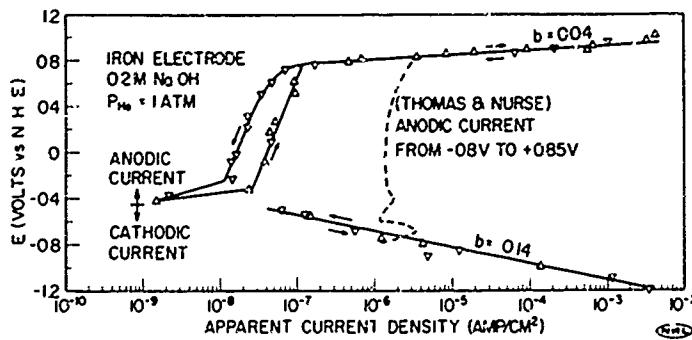


Fig. 3 - Fe potentiostatic polarization curves in 0.2-M NaOH. See Fig. 2 for meaning of symbols. Data from Thomas and Nurse (4) (dashed line).

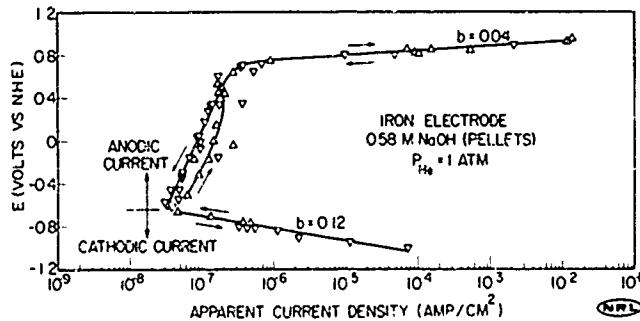


Fig. 4 - Fe potentiostatic polarization curves in 0.58-M NaOH (pellets). See Fig. 2 for meaning of symbols.

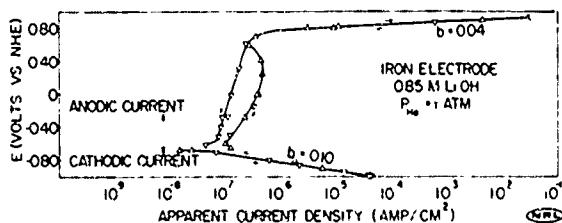


Fig. 5 - Fe potentiostatic polarization curves in 0.85-M LiOH. See Fig. 2 for meaning of symbols.

were very similar. The current densities were slightly lower, the hysteresis loop was narrower, and the changeover from anodic to cathodic current occurred at about 0.55 instead of 0.64 v.

DISCUSSION

There are a number of differences in the results shown in Figs. 2 through 5. Most of them are small and can probably be attributed to the presence of different unremovable impurity levels. The important fact here is that in every case in which the reactable impurities have been reduced to the very low levels represented by these data, the iron behaves as an inert or noble electrode. The current densities are very small and, in the anodic region, primarily represent the oxidation of OH^- and possibly H_2O to oxygen, whereas in the cathodic region, the primary reaction is the reduction of water to hydrogen. The electrodes showed no corrosion or etching either visibly or under low-power microscopic examination. The iron remained bright and shiny throughout the runs without any visible discoloration.

The electrolyte used in obtaining the data in Fig. 4 was prepared from reagent-grade NaOH pellets and had by far the highest level of unremovable impurities. The sodium carbonate content was 65 ppm, which was at least one order of magnitude higher than that in the other Fe/NaOH systems. The data shown in Fig. 2 are believed to be for the purest system. In going from Fig. 2 to Fig. 3 and finally to Fig. 4, it can be seen that the anodic hysteresis loop becomes much narrower. In going from Fig. 2 to Fig. 4, it can be seen that the current density decreases slightly over the major part of the hysteresis loop and the changeover potential from anodic to cathodic current decreases. These differences may be related to the level of unremovable impurities.

It is interesting to note that the width of the hysteresis loop, the shape of the curves, the current densities, and the changeover potential from anodic to cathodic current did not vary appreciably when the electrolyte used to obtain Fig. 2 was diluted in four steps from 0.55- to 0.067-M NaOH or when the LiOH used for Fig. 3 was diluted from 0.85 to 0.34 M. If the differences observed in Figs. 2 through 4 are caused by impurities, it is not the variations in level of impurity that is important but rather the type of impurity or possibly the ratio of impurity to OH^- .

In the case of LiOH the impurity differences in the two samples of metallic lithium used were not as great as for the sodium hydroxide solutions. For LiOH the narrower hysteresis loop was obtained with the solution made from the purer sample. The differences in Li^+ and Na^+ are not great enough to conclude that there is a cation effect. Here again the small differences in behavior are most likely due to the differences in specific unremovable species rather than the total amount of unremovable impurities.

The potentiostatic polarization curve for a Pt electrode in 0.2-M NaOH is given in Fig. 6. When compared to the Fe electrode data (Figs. 2 through 5), the general electrode behavior for Pt and Fe in alkaline solution seem quite similar. Both metals are essentially inert electrode materials on which OH^- and water can be either slowly oxidized to oxygen or reduced to hydrogen, depending on the set potential. The anodic hysteresis effect found on platinum in acid solution (1) was attributed to the dermasorption of oxygen atoms at high positive potentials. Similarly it is believed that the hysteresis found on Pt (Fig. 6) in alkaline solution is also caused by dermasorbed oxygen atoms. The anodic hysteresis found for Fe electrodes (Fig. 2 through 5) can be attributed to either dermasorbed oxygen or to the formation of an iron oxidelike species in the uppermost layers of iron. There is certainly no formation of an extensive bulk iron oxide on the surface. The exact nature of the iron surface, its interactions at the metal/solution interface, or changes in the dermalayer are not known, and further work is required to clarify these very important points.

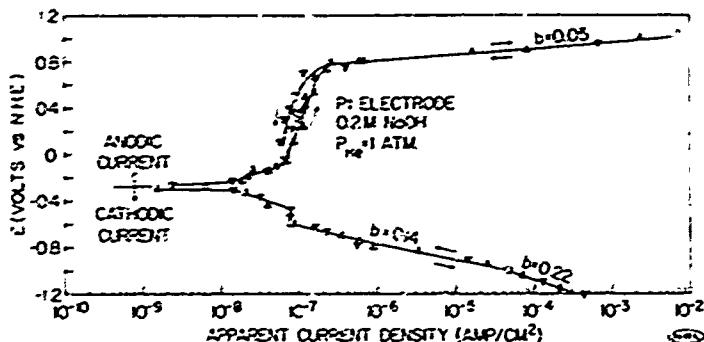


Fig. 6 - Pt potentiostatic polarization curves in 0.2-M NaOH. See Fig. 2 for meaning of symbols.

A question arises as to whether the Pt counterelectrode does contribute Pt which contaminates the Fe electrode, investigated. It has been shown (5) that a pure Fe electrode operating under the conditions described in this paper is a far better catalyst for the hydrogen oxidation reaction than a Pt electrode. A small piece of Pt attached to an Fe wire electrode actually reduced the activity of the Fe for the hydrogen oxidation reaction and gave a very different potentiostatic polarization relation (5). This demonstrated that the contamination of Fe with Pt did not occur in our system.

Potentiostatic current density vs potential curves were determined for an Fe - Pt and an Fe = Pt electrode (an Fe wire shorted outside the cell to an equal size Pt wire) in helium-saturated 0.2-M NaOH. The results are shown in Figs. 7 and 8. Comparing Figs. 7 and 8 with those for pure iron and platinum (Figs. 2 through 6) shows a number of minor differences which indicate that the contamination of an Fe electrode with Pt would have slight effects only. The important thing to note is that, in each of these cases, each electrode is inert and that therefore no appreciable corrosion is taking place. (A small amount of a light-brown corrosion product was found only for the Fe >> Pt electrode at the juncture of the two metals.) Moreover, in each of these cases the current densities have generally the same small values and the polarization curves have essentially the same shapes.

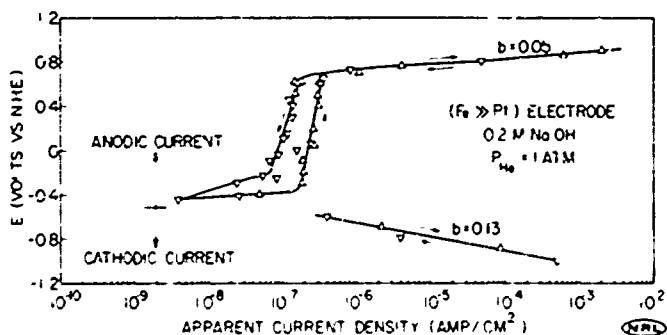


Fig. 7 - (Fe >> Pt) potentiostatic polarization curves in 0.2-M NaOH. See Fig. 2 for meaning of symbols.

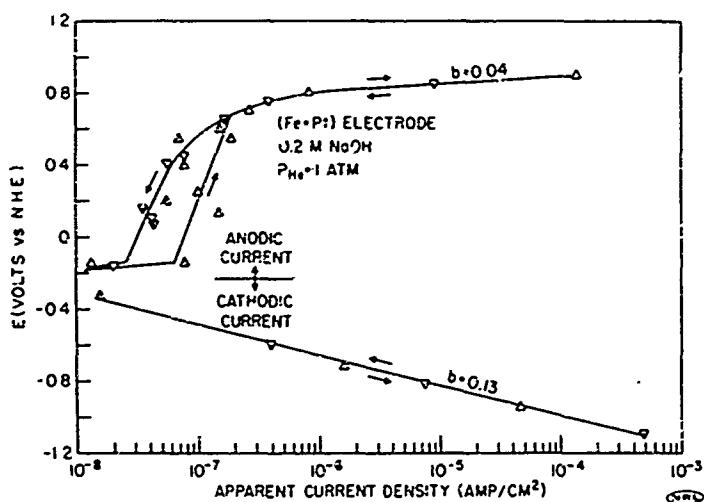


Fig. 8 - (Fe = Pt) potentiostatic polarization curves in 0.2-M NaOH. See Fig. 2 for meaning of symbols.

The major removable trace impurities whose presence may affect potentiostatic polarization curves are oxygen, hydrogen, organic species, and metals. The initial pre-electrolysis in the high-purity closed system used has reduced the level of metallic impurities to at least their level in the electrode material itself. In fact, such impurities at the electrode surface are probably much less than in the bulk of the electrode metal itself. The other impurities were removed by repeating the oxidation or reduction procedure used. The levels of these impurities (other than the amounts of hydrogen or oxygen generated at the applied potentials) were less than 10^{-6} ppm as calculated on the basis of the hydrogen oxidation or oxygen reduction currents required to change the residual current density at a potential near the changeover from net cathodic to net anodic reactions (1). Since the steady-state currents for many inert electrodes, such as iron, are so small in their inactive potential region, they can be completely eclipsed by the electrode reactions due to oxidizable or reducible trace impurities.

To study the effect of a trace impurity that is unremovable but still may alter electrode behavior, experiments were run in which the chloride ion was deliberately added (as NaCl). Figure 9 shows the change in steady-state polarization behavior which the iron electrode underwent upon the addition of 0.2-percent Cl⁻ to 0.2-M NaOH. The Fe electrode with this Cl⁻ addition was covered with a heavy, dark-brown corrosion film, which formed during polarization. The open triangles represent anodic current, and the solid triangles represent cathodic current. The leftmost broken line indicates the variation that occurred between cycles, so there is no clear hysteresis at potentials above 0.3 v. For the decreasing potential sequence at potentials above 0.8 v, the current density remained fairly constant and the activation at -0.1 v was not observed. Thus, there is a large hysteresis loop in which the current density for the increasing potential curve is more than one order of magnitude higher than it is for the decreasing potential curve.

As the potential decreased, the current went from anodic to cathodic at about -0.25 v. When the potential was increased, the current went from cathodic to anodic at about -0.65 v. This large difference in changeover potentials observed in the presence of Cl⁻ is in marked contrast to the purer systems (Figs. 2 through 5), where in any given system the changeover from anodic to cathodic currents and from cathodic to anodic occurred at essentially the same potential.

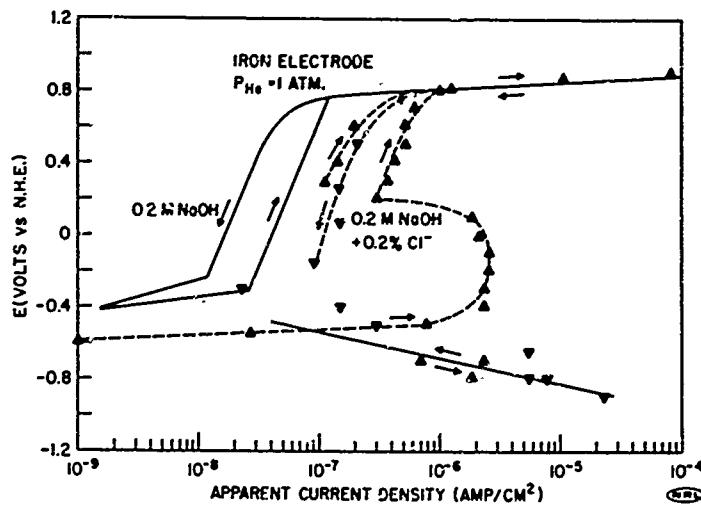


Fig. 9 - Effect of addition of 0.2-percent Cl^- ion on Fe potentiostatic polarization curves in 0.2 M NaOH; Δ anodic current, increasing potential, ∇ anodic current, decreasing potential, \blacktriangle cathodic current, increasing potential, and \blacktriangledown cathodic current, decreasing potential

After the run, the electrode remained at open circuit for about a week in the electrolyte while hydrogen was bubbled through it. During this time the dark-brown oxide film disappeared, leaving a shiny but extensively pitted wire. The steady-state open circuit potential in this hydrogen-saturated solution was -0.682 v. In the absence of added chloride ion, the Fe wire electrode potential was at the equilibrium hydrogen potential of -0.78 v (5).

In the increasing potential sequence shown in Fig. 9, the Fe electrode does undergo normal passive behavior, the potential of highest activity for iron corrosion being about -0.1 v. An attempt was made to duplicate the results of Thomas and Nurse (4) shown in Fig. 3. Their data were taken 5 minutes after a change in potential. Using a similar technique of taking readings 5 minutes after a change in potential in the chloride containing NaOH, the results shown in Fig. 10 were obtained. Under these conditions passive behavior similar to that found by Thomas and Nurse was observed.

It has been shown that the high-purity Fe/NaOH system very effectively oxidizes hydrogen (5). The potentiostatic polarization curve for this system is shown by the broken line in Fig. 11. The curve for the identical system to which 0.2-percent Cl^- was added is shown as a solid line. The variations of the increasing and decreasing potential data about this solid line are small, which is in sharp contrast to the large variations obtained in an inert helium atmosphere (Fig. 9). This indicates that the fraction of the current density in the Cl^- -contaminated solution that represents corrosion is much less than the fraction that represents oxidation of hydrogen. In the high-purity system, the current density is so high that it must be essentially all from hydrogen oxidation.

Chloride contamination makes iron an extremely poor catalyst for the hydrogen oxidation reaction. Firstly, the iron is no longer a reversible hydrogen electrode and even at very low current densities the polarization potential required for hydrogen oxidation is over 0.2 v above the reversible hydrogen potential. Secondly, at comparable potentials the chloride-free NaOH oxidizes hydrogen about 10^3 times faster. In terms of fuel cell operation, which would be at low polarization potentials, the chloride-free system is infinitely better.

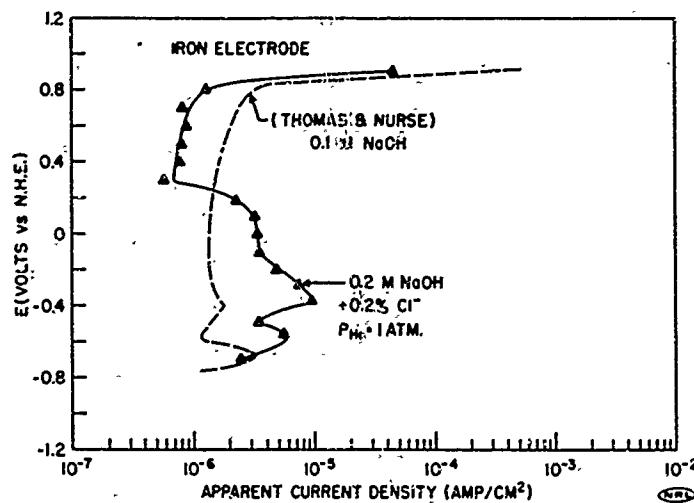


Fig. 10 - Comparison of Fe (chloride contaminated) potentiostatic polarization curves with results of Thomas and Nurse (4). Data points taken 5 min after each potential setting. Δ increasing potential sequence.

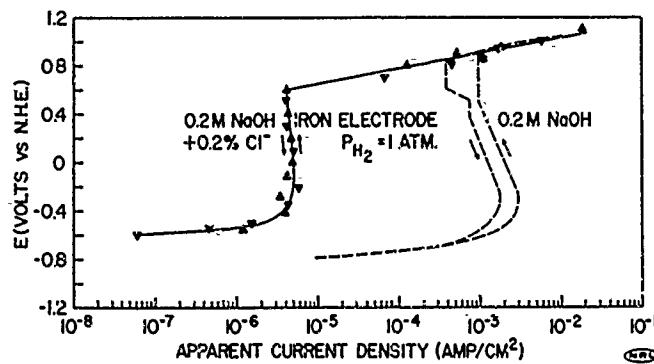


Fig. 11 - Rates of hydrogen oxidation on Fe under potentiostatic control in 0.2-M NaOH and the effects of chloride ion contamination. See Fig. 2 for meaning of symbols.

Another important consequence of the data shown in Fig. 11 is that the passivation (reversal of $dE/d\log i$) of the hydrogen oxidation reaction which occurs in the pure NaOH at about -0.3 v is essentially nonexistent in the chloride-contaminated NaOH. This confirms the hypothesis (6) that passivation can be caused by a reduction in the active electrode area but is primarily due to a poisoning of catalytically active sites which causes large changes in the heat of activation for the hydrogen oxidation reaction of the electrode surface. In an iron electrode in alkali solution, the chloride ion and the resultant corrosion products induced by its presence so completely retard the hydrogen oxidation reaction that the catalytic properties of the electrode are virtually nonexistent and therefore further adsorption of anions at more noble potentials does not cause significant active area changes or passivation of the hydrogen oxidation reaction. In the chloride-free NaOH, the passivation of the hydrogen oxidation is rather small and is most likely primarily an effect of reduction in the active electrode area caused by anion adsorption (4).

CONCLUSIONS

In the high-purity alkaline solutions used, iron does not significantly corrode or show passive behavior (defined (6) as a condition in which the net reaction rate decreases with an increase in potential) over a wide range of concentrations and potentials. Iron acts like an inert noble metal similar to platinum rather than as a passivated metal. Depending on potential the primary reactions are the oxidation or reduction of OH⁻ and water. This does not mean that the iron electrodes used do not have species other than iron atoms on their surfaces. The surface state of the iron is unknown. Hysteresis effects were observed upon decreasing the potential sequence after high noble potentials were applied. This caused a reduction in OH⁻ oxidation rates which are in turn caused by changes in the dermalayer of iron.

Iron in the high-purity, closed system is an excellent catalyst for the electrochemical oxidation of hydrogen, being appreciably superior to Pt (4). Chloride ion causes extensive iron corrosion, completely changes the potentiostatic polarization relation, and does show passive behavior. Chloride ion virtually destroys the catalytic properties of the Fe electrode for the hydrogen oxidation reaction.

The presence of reactable impurities was shown to strongly change the electrochemical behavior of iron in alkali solution. The high-purity, closed electrochemical system successfully eliminated the major effects of such impurities.

Even though there were some variations among the high-purity Fe-alkaline systems investigated, each system had approximately the same shape curves and the same low activity for both water oxidation and reduction except at extremes in anodic or cathodic potentials, respectively.

The variations in behavior for the various Fe/alkaline systems studied may be largely caused by the unremovable impurities. Probably the most important of these would be halide ions. Such impurities as carbonates, silicates, and sulfates, which are unremovable, may have caused minor differences in various runs. However, it is felt that the effects of the major anion, OH⁻, would override those of other trace inert anions.

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Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified
2b. GROUP		
3. REPORT TITLE POTENTIOSTATIC CURRENT-POTENTIAL MEASUREMENTS ON IRON AND PLATINUM ELECTRODES IN HIGH-PURITY CLOSED ALKALINE SYSTEMS		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) An interim report; work is continuing on the problem.		
5. AUTHOR(S) (First name, middle initial, last name) Clarence M. Shepherd and Sigmund Schuldiner		
6. REPORT DATE August 26, 1968	7a. TOTAL NO. OF PAGES 18	7b. NO. OF REFS 6
8a. CONTRACT OR GRANT NO. NRL Problem M04-08	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6748	
b. PROJECT NO. ARPA Order 878	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.		
d.		
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency of the Department of Defense, Washington D.C. 20301
13. ABSTRACT Potentiostatic polarization curves were determined for Fe, Pt, and combinations of Fe and Pt electrodes in NaOH and LiOH solutions saturated with helium. With the high-purity, gastight system used, the level of reactable impurities was reduced to about 10^{-6} ppm. Under these conditions the primary reactions are, depending on potential, the oxidation or reduction of OH^- and water. Iron does not significantly corrode or show a decrease in reaction rate with an increase in potential (passivate). Iron acts like an inert noble metal similar to platinum.		
Chloride ion causes extensive iron corrosion, completely changes the potentiostatic polarization behavior, and does cause typical passive behavior. Under high-purity conditions, iron is an excellent catalyst for the hydrogen oxidation reaction; the presence of chloride ion, however, almost completely destroys the catalytic properties of Fe for this reaction.		
Unreactable and unremovable impurities such as carbonates, silicates, sulfates, apparently do not have major effects on the polarization behavior of Fe. The major anion, OH^- , appears to dominate the inert anion effects. ()		
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